Dienes

*Reactions of Dienes*

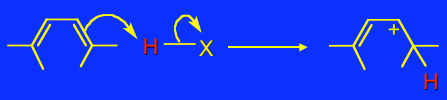
*isolated dienes:* double bonds react independently of one another

*conjugated dienes:* reactivity pattern requires us to think of conjugated diene system as a functional group of its own

*cumulated dienes:* specialized topic

*Addition of Hydrogen Halides*
*to*
*Conjugated Dienes*

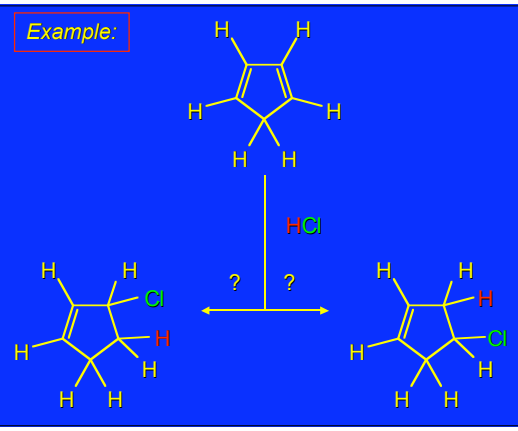
*Electrophilic Addition to Conjugated Dienes*



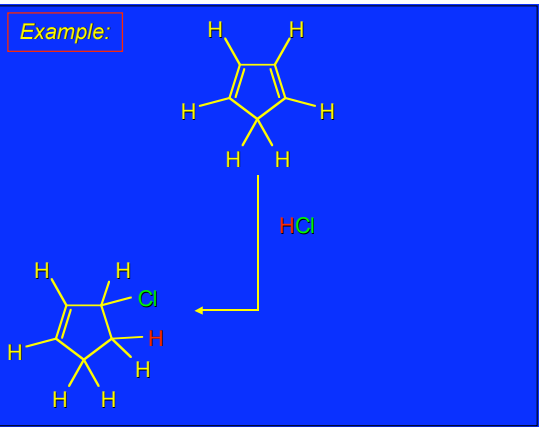

Proton adds to end of diene system

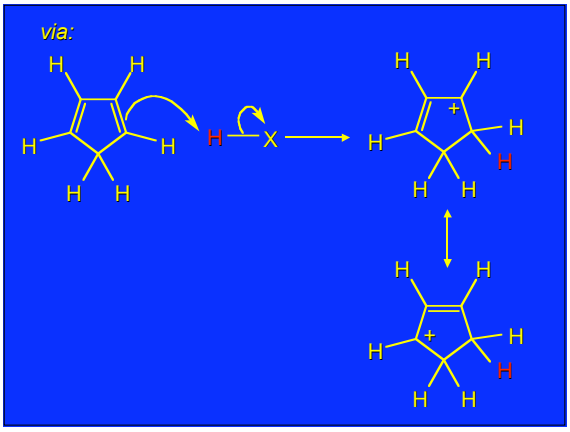
Carbocation formed is allylic

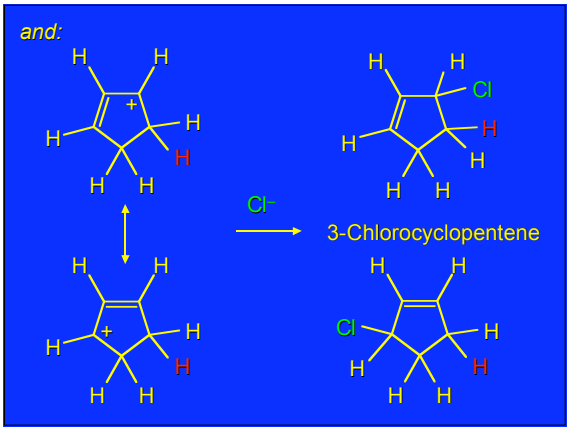
*Example:*

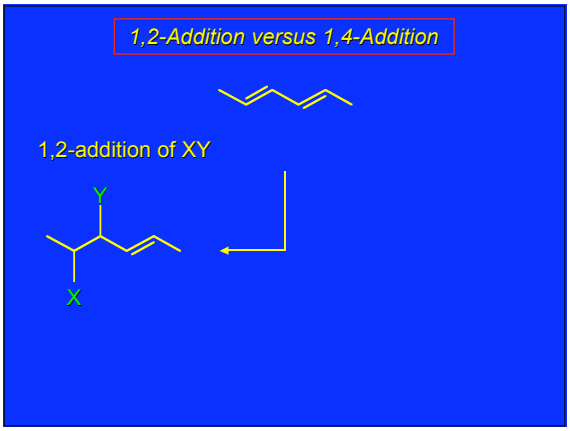


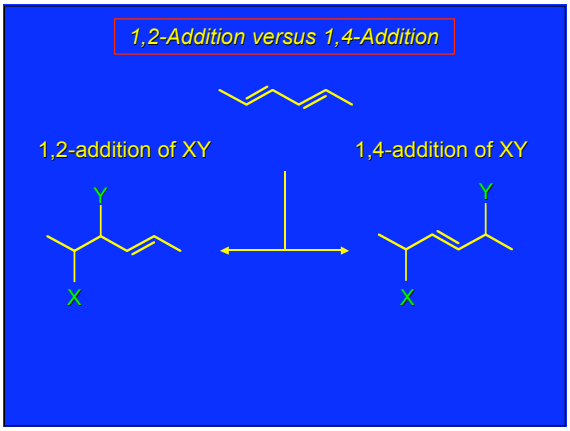

*Example:*

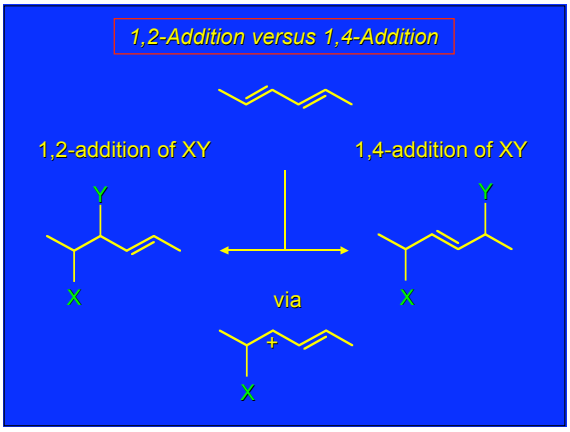


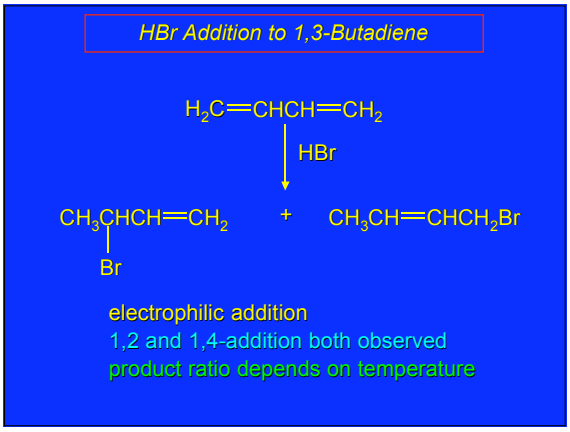

via:
H
X


and:
Cl⁻
3-Chlorocyclopentene


1,2-Addition versus 1,4-Addition
1,2-addition of XY
Y
X


1,2-Addition versus 1,4-Addition
1,2-addition of XY
1,4-addition of XY
Y
X

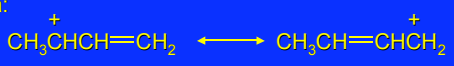

1,2-Addition versus 1,4-Addition
1,2-addition of XY
1,4-addition of XY
Y
X
via


HBr Addition to 1,3-Butadiene
H2C=CHCH=CH2
HBr
CH3CHCH=CH2
Br
+
CH3CH=CHCH2Br
electrophilic addition
1,2 and 1,4-addition both observed
product ratio depends on temperature

*Rationale*

3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.


via:




*Rationale*

3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.


formed faster

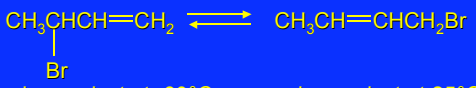
*Rationale*

1-Bromo-2-butene is more stable than 3-bromo-1-butene because it has a more highly substituted double bond.


more stable

*Rationale*

The two products equilibrate at 25°C. Once equilibrium is established, the more stable isomer predominates.



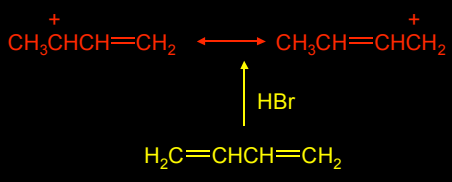

major product at -80°C (formed faster)

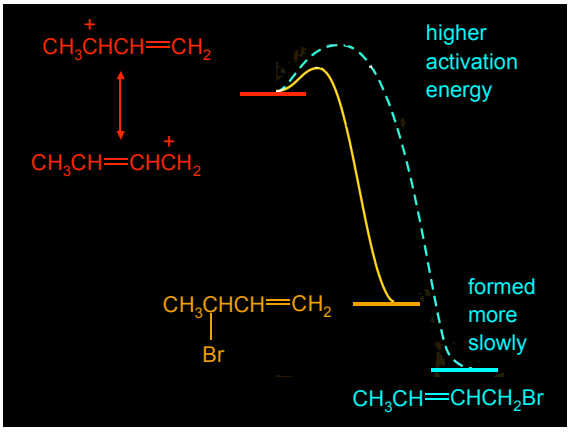
major product at 25°C (more stable)

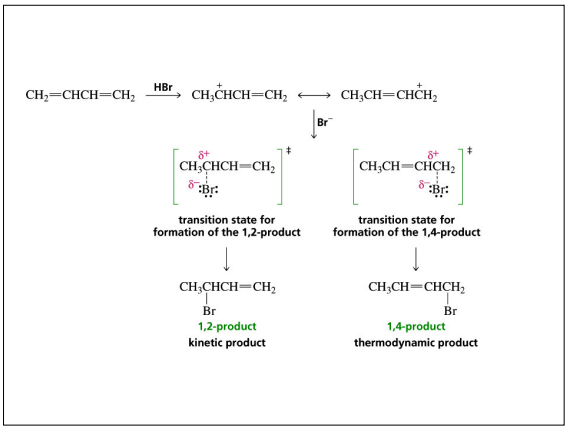
*Kinetic Control versus Thermodynamic Control*

Kinetic control: major product is the one formed at the fastest rate

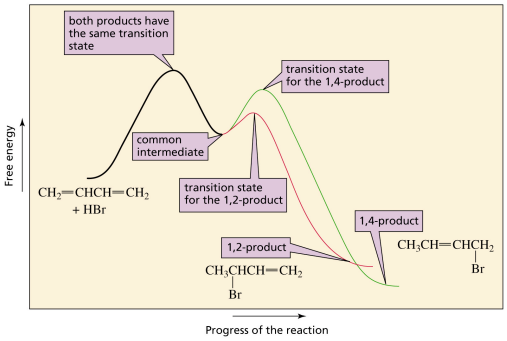
Thermodynamic control: major product is the one that is the most stable






Consider the reaction coordinate diagram …

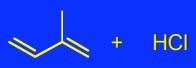



*Problem*

Addition of hydrogen chloride to 2-methyl-1,3-butadiene is a kinetically controlled reaction and gives one product in much greater amounts than any isomers. What is this product?


*Problem*

Think mechanistically.




Protonation occurs:

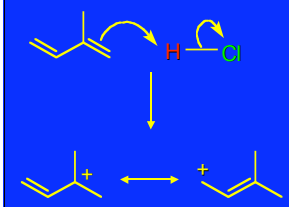
at end of diene system

in direction that gives most stable carbocation

Kinetically controlled product corresponds to attack by chloride ion at carbon that has the greatest share of positive charge in the carbocation

*Problem*

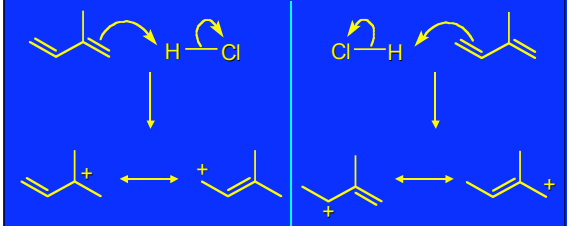
Think mechanistically




one resonance form is tertiary carbocation; other is primary

Problem

Think mechanistically

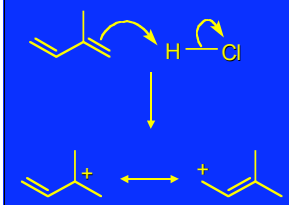


one resonance form is tertiary carbocation; other is primary

one resonance form is secondary carbocation; other is primary

Problem

Think mechanistically



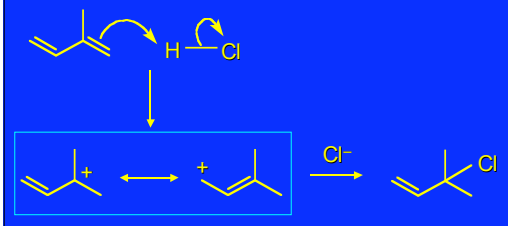
one resonance form is tertiary carbocation; other is primary

More stable carbocation

Is attacked by chloride ion at carbon that bears greater share of positive charge

Problem

Think mechanistically



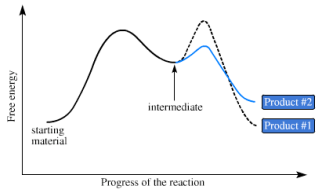
one resonance form is tertiary carbocation; other is primary

major product

The 1,4-addition product is NOT always the thermodynamic product …


Always compare the intermediates and products to assign the kinetic (PATHWAY) and the thermodynamic product ( Lower ENERGY STATE)

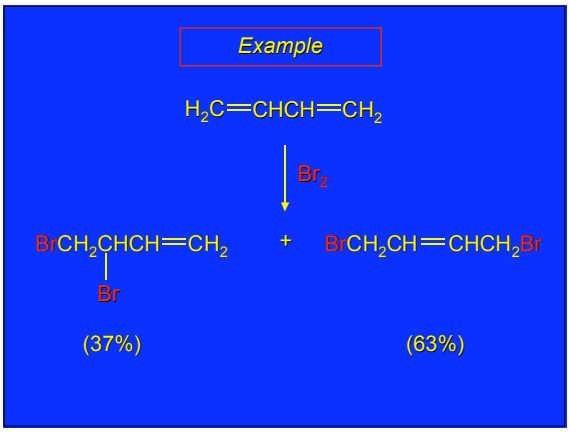
Click "Product #1" or "Product #2" to label the KINETIC product.




Example 1

Halogen Addition to Dienes

gives mixtures of 1,2 and 1,4-addition products


Example
H2C=CHCH=CH2
Br2
BrCH2CHCH=CH2
Br
+
BrCH2CH=CHCH2Br
(37%)
(63%)